Polymolecularity and molecular shape of methyl methacrylate polymers and their dependence on the conditions of polymerization[1]

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The present paper is, in the main, a summary of the following reports which will subsequently be referred to by the Roman numerals I—V. Some further data have been added.

I. *Eriksson, A. F. V.* Acta Chem. Scand. *3* (1949) 1.
II. *Eriksson, A. F. V.* Acta Chem. Scand. *7* (1953) 377.
III. *Eriksson, A. F. V.* Acta Chem. Scand. *7* (1953) 623.
IV. *Eriksson, A. F. V.* Acta Chem. Scand. *10* (1956) 360.
V. *Eriksson, A. F. V.* Acta Chem. Scand. *10* (1956) 378.

Introduction

The reaction kinetics for the polymerization of methyl methacrylate was first investigated by *Melville*,[9–12] *Norrish*,[14–16] and *Schulz*.[19–22] *Melville* studied the gas phase photopolymerization. *Norrish* and *Schulz*, however, were mainly interested in the mechanism of the polymerization of the monomer in the pure liquid phase (bulk polymerization) and in solution. Using benzoyl peroxide as initiator, it was found that the polymerization reaction was of first order with respect to the monomer in the earliest part of the reaction. During this stage, the rate of reaction was found to be proportional to the square root of the concentration of initiator.[15, 22]

However, after 10 to 20 per cent conversion, the reaction is "almost explosive" in the bulk polymerization, and the remaining monomer can be polymerized in a few minutes. This increase in rate was first attributed to local overheating[14] due to the liberated heat of reaction and to the poor heat conductivity of the reaction mixture. The heat of polymerization has been determined to be 13—14 kcal/mol.[27, 5] An increase in temperature of about 100° C was also reported by both *Norrish*[14] and *Schulz*.[22] *Schulz* and *Blaschke*[20, 21] sought to explain the acceleration in the polymerization rate by assuming that the rate of initiation of growing polymer radicals increased after the first stationary state period.

That neither of these explanations can be correct was shown by *Norrish* and *Smith*.[16] In a polymerization experiment with methyl methacrylate in narrow glass ampoules, at a temperature of 25° C, they were able to maintain isothermal condition throughout the reaction, yet the con-

[1] Inaugural dissertation.

version versus time curve had the same shape as at higher temperatures. They also found that the average molecular weight of the polymer increased at the same time as the increase in polymerization rate occurred. This would be impossible if an increase in the initiation of growing radicals caused the acceleration in rate.

Norrish and *Smith* ascribed both the increase in reaction rate and the increase in average molecular weight of the formed polymers to a drop in the rate of chain termination. The growth of the polymer radicals is stopped by mutual termination, either by disproportionation between two radicals or by combination of two radicals to one single dead molecule. The deactivation must, therefore, be rendered more difficult when the reaction medium grows more viscous, as it will be more difficult for the growing centers to make contact and react with each other.

This theory of *Norrish* and *Smith* was founded on the following observations. According to *Norrish* and *Brookman*,[14] the average molecular weight increases approximately in proportion to the amount of polymer formed. Furthermore, the increase in rate of reaction occurs at a higher degree of conversion if the polymerization is performed at a higher temperature, or with a larger amount of initiator. In both these cases a polymer with a lower molecular weight is formed and, hence, the viscosity of the reaction mixture is lower.

To test the proposed explanation of the accelerated reaction rate and the increase of average molecular weight, *Norrish* and *Smith* performed a series of polymerization experiments in a number of different diluents. They showed that if the diluent was a precipitant or a poor solvent for the polymer, the viscosity of the reacting mixture was very high, and the acceleration in rate and the increase in average molecular weight occurred faster. On the other hand if the diluent was a good solvent, and consequently the viscosity low, the explosive stage was more or less eliminated.

Since the monomer is a good solvent, this consideration may also be applied to the bulk polymerization. In a good solvent, the polymer radicals will be extended, giving good opportunities for chain ends to react with one another. In a poor solvent, the polymers will be more tightly coiled, and the active ends of the molecules shielded from each other. As monomer molecules still can easily diffuse into the coiled polymers, the rate of propagation will be less influenced by the change in viscosity. The increase in both reaction rate and average molecular weight, can, therefore, be explained by an increase in mean life time of the radicals.

In an investigation of the mass distribution for some commercial poly (methyl methacrylate)s, *Kinell*[7] obtained very broad mass frequency curves with three maxima. The great heterogeneity of the bulk polymer will be a natural consequence of the increase in the average molecular weight. This will be more clear if one converts the average molecular weights into molecular weight increments, this quantity being defined as the mean molecular weight of all the polymer molecules formed at a certain degree of conversion.[29] This method has been used by *Schulz*[22] and *Eriksson* (I).

POLYMOLECULARITY AND MOLECULAR SHAPE OF METHYL METHACRYLATE POLYMERS AND THEIR DEPENDENCE ON THE CONDITIONS OF POLYMERIZATION

INAUGURAL DISSERTATION

BY

A. FREDRIK V. ERIKSSON

FIL. LIC., KALM.

BY DUE PERMISSION OF THE PHILOSOPHICAL FACULTY OF THE UNIVERSITY OF UPPSALA, TO BE PUBLICLY DISCUSSED IN THE LECTURE HALL OF THE INSTITUTE OF CHEMISTRY, MAY 23 1956 AT 10 A. M., FOR THE DEGREE OF DOCTOR OF PHILOSOPHY. IN ADDITION TO THIS SURVEY THE PAPERS REFERRED TO BY THE ROMAN NUMERALS I—V GIVEN AT THE BEGINNING OF THIS PAPER WILL BE PUBLICLY DISCUSSED.

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A very valuable confirmation of the viscosity-chain termination theory of the acceleration of methyl methacrylate polymerization has been given by *Trommsdorff et al.*[28] They found that dissolved cellulose tripropionate has the same effect on the polymerization rate as the presence of the polymer itself. They also demonstrated that immobilization of the growing radicals by the presence of cross linking agents increased the polymerization rate. *Trommsdorff et al.* also investigated the change in molecular weight distribution with the degree of conversion in the case of suspension polymerization. For a degree of conversion of 23 per cent, the mass frequency function was rather narrow and showed only one maximum. At a degree of conversion of 95 per cent, the mass frequency curve was broad and had two maxima. They also determined the mass distribution for a bulk polymer at the end of the polymerization, the mass frequency curve being broad and doubly peaked. The maxima were, however, not so pronounced as previously reported by *Kinell.*

The dependence of the mass distribution, in poly (methyl methacrylate) prepared in bulk, on the degree of conversion has simultaneously been investigated by *Smets et al.*,[25] and *Eriksson* (I). They reported a single peaked mass frequency function for polymers at low degrees of conversion, corresponding to the stationary state of the polymerization reaction. For higher degrees of conversion, they obtained two maxima in the mass frequency curves. The two maxima are most pronounced for medium degrees of conversion, corresponding to the middle part of the explosive stage. At higher degrees of conversion, the different peaks appear to be more or less blurred out. The results obtained were interpreted with the Norrish-Smith theory by both authors.

A further support for this theory is the results obtained by *Smets et al*,[25] in investigating the influence of inhibitor on the mass distribution. They showed that nitrobenzene both suppresses the acceleration in the polymerization rate, and causes a smaller second maximum in the mass frequency curve—the molecules of inhibitors and chain transfer agents being so small that their activity will not be markedly influenced by the increasing viscosity.

Mass distribution curves for poly (methyl methacrylate)s prepared by redox polymerization in aqueous solution, have been determined by *Evans et al.*,[1–3] and *Eriksson* (II). In this case, the reaction medium does not undergo so great a change as in the case of bulk polymerization. The distributions obtained are, in agreement herewith, narrower and do not change very much with the degree of conversion (II).

In two later papers, one by *Billmeyer* and *Stockmayer*[4] and the other by *Harris* and *Miller*,[6] the existence of a multiply peaked mass frequency curve for poly (methyl methacrylate) has been suspected. In the first of these investigations a quantity,

$$z = x\,(M_x - M_w)\,\frac{1}{M_w}$$

is introduced, x being the weight fraction of the total precipitate in a

precipitation fractionation, M_x and M_w the weight average molecular weight of, respectively, the precipitate and the initial samples.

From the maximum value of z, it is possible to calculate the ratio between the weight average, M_w, and the number average, M_n, of the unfractionated sample. In this way, it is shown that the degree of polydispersity increases with the degree of conversion in the case of bulk polymerization of methyl methacrylate (photopolymerization). The ratio M_w/M_n changes from 2 to 6—10. *Lauterbach*[4] found a value of M_w/M_n between 7 and 8 for peroxide initiated high conversion poly (methyl methacrylate) in a fractional precipitation experiment. This is in agreement with previously discussed investigations. *Stockmayer et al.*, however, state that they never obtained a doubly or multiply peaked frequency curve. From the experimental data given, it seems probable, however, that these authors have happened to avoid investigating polymers of medium degree of conversion, where the doubly peaked distribution is most pronounced.

In the second paper by *Harris* and *Miller*, the molecular weight distributions of several different poly (methyl methacrylate)s are determined with the aid of a turbidimetric method. These authors never found a doubly peaked distribution, all polymers having a ratio of weight average to number average molecular weight of 1.5 to 2.2. The number average molecular weights are, in all cases, between 50,000 and 100,000. Most of these polymers seem to be granular polymers, and at least one is prepared in the presence of a chain transfer agent. Two samples are, however, polymerized in bulk with photoinitiation. Even these polymers have very low molecular weights. It appears probable, that the polymerization has proceeded without a marked Norrish-Smith effect. The molecular weights, the presence of chain transfer agents, and the polymerization technique for most of the samples, are unfavourable for the occurrence of this effect.

Present work.—The present investigation is a continuation of the work reported in ref. I and II. Some additional distributions have been determined, in order to follow the change in the shape of the distribution during the different stages of the polymerization reaction. The form of the molecules will also be considered.

Experimental

Polymerization.—Previously reported determinations of the mass distributions (I) of poly (methyl methacrylate)s were obtained for polymers polymerized at 80° C. In order to be certain of avoiding local overheating during polymerization, and possible disturbances in the distribution of mass from this, a lower temperature was chosen for these experiments, namely 60° C.

The monomer was carefully rectified by redistillation at low pressure. The correct amount of benzoyl peroxide was introduced in the reaction vessel as a benzene solution, whereafter the benzene was sublimed off. The capacity of the glass reaction ampoules was about 100 ml. The form of the ampoules was such, that it was possible to introduce the monomer without this coming into contact with the initiator.

For each experiment, about 30 ml of highly purified methyl methacrylate was distilled directly into the reaction vessel, at low pressure, and sealed off. Before this fin al distillation, the whole apparatus had been evacuated and flushed with oxygen-

free nitrogen several times, and sealed off from the vacuum pump. The polymerization was performed in a water thermostat, and the reaction vessel rotated during the whole time in order to avoid overheating. The reaction mixture was diluted, or dissolved, with acetone after the polymerization was stopped, and the polymer isolated by precipitation in methanol. The polymer was dried in vacuum at room temperature to constant weight. The polymerization conditions, and the degrees of conversion obtained, are summarized in Table 1 and Fig. 1.

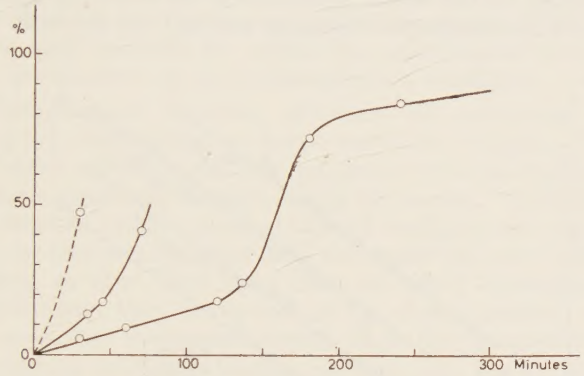

Fig. 1. The degree of conversion as a function of time.

Table 1. Showing the polymerization conditions for the different polymers.

Polymer	Polymerization temperature	Initiator concentration mg/g monomer	Polymerization time minutes	Degree of conversion %	Intrinsic viscosity
B(711)	60° C	5.36	30	5.18	1.04
B(708)	60° C	5.29	60	9.07	0.95
B(704)	60° C	5.14	120	18.1	—
B(709)	60° C	5.24	136	24.3	1.20
B(720)	60° C	5.26	180	72.4	—
B(723)	60° C	5.30	240	84.4	—
B(703)	60° C	5.36	(468 hours)	90.1	—
B(712)	80° C	5.33	30	47.4	0.59
B(714)	80° C	1.08	35	13.7	0.90
B(716)	80° C	1.07	45	17.5	—
B(713)	80° C	1.06	70	41.3	1.11

Fractionation.—The fractionation was performed by fractional precipitation from acetone solution, the initial concentration of the polymer being 0.5 g per 100 ml. Petroleum ether was used as precipitant. This was added gradually, at 20.0° C, with constant stirring, until a turbidity appeared. The temperature of the thermostat was then raised until the solution was again completely clear, after which the stirrer was stopped and the temperature was allowed to fall slowly to 20.0° C during the night.

Later, when the necessary amount of petroleum ether required for a fraction was known, the addition of precipitant was made at so high a temperature that no turbidity appeared before the temperature was lowered. The precipitant formed was recovered by decanting the solution, and was dissolved in acetone—from which it was reprecipitated with an excess of methanol. The fraction obtained was dried *in vacuo* at room temperature, until it had reached constant weight. The degree of reproducibility attainable by this procedure has previously been investigated (see [II]).

Results

The shape of the polymer molecules.—The hydrodynamic behaviour of poly (methyl methacrylate) molecules has been treated in a previous paper (V). It was shown there, that polymer molecules obtained by bulk polymerization exhibit two peculiar properties. Contrary to what ought to be expected from the Flory theory for linear flexible chain molecules, there is a break in the linear relationship between log s_0 and log $[\eta]$, where s_0 is the sedimentation constant and $[\eta]$ the intrinsic viscosity of

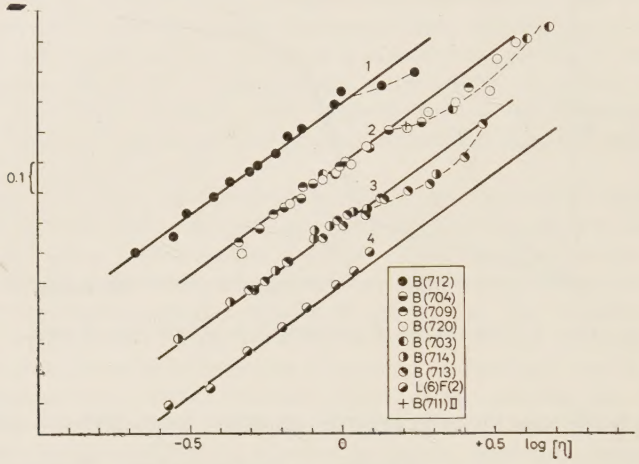

Fig. 2. Showing the relationship between log s_0 and log $[\eta]$ for the different fractions. Points from different polymerization conditions have been displaced from one another, in order to avoid confusion. The four solid lines are the same in all cases. Polymerization conditions:

Curve 1	Polymerization temperature	80° C.	Initiator concentration	high	
» 2	»	»	60° C.	»	»
» 3	»	»	80° C.	»	» low
» 4	Redox polymerization				

a fraction. It was further found that the ratio $s_0 [\eta]^{1/3}/M^{2/3}$ showed a definite trend to increase with increasing molecular weight M, even in the region where log s_0 is a linear function of log $[\eta]$.

The relationship between sedimentation constant and intrinsic viscosity is graphically illustrated in Fig. 2. The four curves represent the data obtained under different polymerization conditions with respect to initiator concentration, polymerization temperature, and polymerization technique. The points from the different experiments have been displaced from one another, in order to avoid confusion. The solid lines are the same in each case, and correspond to the equation $\log s_0 = 0.739 \log [\eta] + 1.29$. The constants in this expression have been obtained by applying the method of least squares to all points in the region where the linear relationship holds (V).

There is a connection between the degree of conversion and the appearance of the break in the log s_0 — log $[\eta]$ plot. This can be seen from curves two and three, that give data from bulk polymerization at a temperature of 60° C and 80° C, respectively. The points for the highest molecular weight fractions, obtained from polymers at higher degrees of conversions, tend to lie below the straight line. But even for a degree of conversion of only 5 per cent B(711), fraction two lies a little below the straight line—in the figure, represented by a cross. All points for low molecular weight fractions lie, within the experimental accuracy, on the same line, irrespective of the polymerization condition.

A high temperature, however, displaces the non-linear part of the log s_0 — log $[\eta]$ relationship to lower molecular weights. The direction of the deviation indicates that the polymers with the highest molecular weights, which have been formed during the second, "explosive", stage of the polymerization, have a more elongated configuration than the others. The reason for this can be either that the molecules have been connected by branching, or that they have been so tightly entangled during the polymerization that they never can get rid of one another. More experiments are necessary to decide between these two possibilities.

For the highest molecular weight fractions, the log s_0 — log $[\eta]$ curve is found to turn back to the straight line. This can be understood if the largest molecules are still more branched or the aggregates consist of still more molecules. This would, again, give a more spherical shape to the particles.

A smooth s_0 — $[\eta]$-curve has been found by *Meyerhoff*[13] for poly (methyl methacrylate). The different fractions were, however, not prepared by the same polymerization technique in all cases. This fact, and the circumstance that the method of fractionation can have given different degrees of homogeneity to the fractions, can be the reason why no irregularity was observed. *Kinell*,[7] on the other hand, has reported a peculiar dependence of s_0 on $[\eta]$ for some poly (methyl methacrylate)s. This investigation was, unfortunately, made on some commercial bulk polymers of unknown origin, which fact would make a comparison difficult.

In the previously mentioned paper (V), it was shown that the Flory theory for flexible chain polymers was substantially applicable to poly (methyl methacrylate) molecules dissolved in ethyl acetate, if molecules from the early part of the polymerization reaction are considered. There were, however, small but systematic deviations from the values predicted by the theory. There was found, for instance, a definite trend for the ratio, $s_0 [\eta]^{1/3}/M^{2/3}$, to increase with increasing molecular weight.

In order to eliminate this discrepancy between the experimental results and the theory, an attempt has been made to substitute for the equivalent sphere used by *Flory*, an equivalent ellipsoid of rotation. Instead of the equations

$$[\eta] = \frac{3\,\Phi}{4\,\pi} \cdot \frac{V_e}{M} \qquad (1)$$

and

$$f = \eta_0 P \left[\frac{3\,V_e}{4\,\pi}\right]^{1/3} \tag{2}$$

where V_e is the volume of an equivalent sphere, the following expressions for the intrinsic viscosity, $[\eta]$, and the frictional constant, f, at infinite dilution, will be obtained:

$$[\eta] = \frac{3\,\Phi}{4\,\pi}\left[\frac{\nu}{2.5}\right]\left[\frac{V_e}{M}\right] \tag{3}$$

and

$$f = \eta_0 P \left[\frac{3\,V_e}{4\,\pi}\right]^{1/3} \frac{1}{F} \tag{4}$$

where V_e now is the volume of an equivalent ellipsoid of rotation.

The constants Φ and P will, as previously in equations (1) and (2), take into account the fact that the real molecule does not have the same well defined surface as the equivalent sphere or ellipsoid, which are assumed to be rigid, and impermeable to the solvent. In the last two equations, ν and F are shape factors which depend on the axial ratio, p, of the ellipsoid. The quantity ν has been calculated by *Simha*,[24] and values of ν as a function of p, for prolate and oblate ellipsoids, have been tabulated by *Mehl*, *Oncley* and *Simha*.[8] The quantity F has been calculated by *Perrin* and is tabulated in the monograph by *Svedberg* and *Pedersen*.[26]

This method of approximating the hydrodynamic behavior of macromolecules with an equivalent ellipsoid has previously been used by *Scheraga* and *Mandelkern*.[18] They give expressions for $[\eta]$ and f, identical with equations (3) and (4) in all except that the equations do not contain the factors Φ and P, accounting for the surface effects, which have to be introduced here. If equations (3) and (4) are combined with the Svedberg equation,

$$s_0 = \frac{M\,(1 - V\varrho)}{Nf} \tag{5}$$

one obtains

$$\frac{s_0[\eta]^{1/3}}{M^{2/3}}\,\frac{\eta_0 N}{(1 - V\varrho)} = \Phi^{1/3} P^{-1} \left[\frac{F^3\nu}{2.5}\right]^{1/3} = \beta \tag{6}$$

It will be assumed here that Φ and P can be treated as constants if the axial ratio, p, does not change too much. The ratio,

$$\gamma = \frac{\beta \text{ ellipsoid}}{\beta \text{ sphere}}$$

will then depend only on the functions F and ν of the axial ratio of the ellipsoid. γ can be calculated from the tables given by *Mehl et al.* and by *Perrin* in the monograph by *Svedberg* and *Pedersen*, or from Table 1 given by *Scheraga* and *Mandelkern*.

The following mean values of β were obtained for poly (methyl methacrylate) dissolved in ethyl acetate, namely, 2.37, 2.41, and 2.52 for the molecular weight intervals $< 2.5 \times 10^5$, 2.5×10^5 to 5×10^5 and $> 5 \times 10^5$, respectively. The number of fractions in each region was respectively 9, 13 and 12. If the polymer molecules in the molecular weight region $< 2.5 \times 10^5$ are assumed to be spherical—that is $\beta_{\text{sphere}} = 2.37$ the equivalent ellipsoids of the molecules in the other two regions will have axial ratios of the semi-axis of revolution to the equatorial radius of 3—4, and 5, respectively. Because of the simplification of the assumptions, the figures are certainly not quite true, but they give an idea of the change in configuration of the polymer chains as the molecular weight increases.

It is difficult to say anything about the reason for the more elongated shape of the larger molecules. If, however, the steric hindrances in the larger polymer radicals are sufficiently great, each radical would partly retain the spherical shape it got in the moment of growth. In the case of deactivation of the growing radicals by combination, the dead molecules would be more or less like a pair of spheres, giving a more elongated shape to the larger polymer molecules. The effect can also, possibly, have been caused by an increasing degree of branching with increasing molecular weight.

There is, however, also a third possibility. It is not necessary to assume an ellipsoidal configuration of the molecule to explain the trend in the ratio $\frac{s_0[\eta]^{1/3}}{M^{2/3}}$. This trend can also be interpreted by the Debye-Bueche or the Kirkwood-Riseman theories. In the first of these the molecule is treated as a sphere that is partly permeable to the solvent. It has been shown by *Peterlin*[17] that an increase in the ratio $\frac{s_0[\eta]^{1/3}}{M^{2/3}}$ means an increasing permeability of the sphere to the solvent so if the molecules are assumed to behave as spheres, according to the assumptions of the Debye-Bueche theory the unexpected conclusion must be that the larger molecules are most permeable, that is, have the smallest "shielding ratio". It seems to be most probable that the molecules become both more elongated and at the same time less dense with increasing molecular weight.

Construction of mass distribution curves. — All measurements on the fractions have been made in ethyl acetate solutions at 20° C. For details concerning the determination of intrinsic viscosities, sedimentation constants and diffusion constants, reference may be made to reference (V). In constructing a curve of mass distribution, it has -in accordance with the usual method[23]- been assumed that half of the mass of a fraction has a molecular weight (or intrinsic vicosity) lower than the average value determined for the fraction, the other half having a higher value, and that the fractions do not overlap. This method does not take the polydispersity of the fractions into account and it can, therefore, give uncertain results when the fractions are broad.

A more satisfactory method for constructing the mass distribution

curve has been given by *Rånby*, for the case where the $\left(\frac{dB}{dx}\right)$-values of the fractions are known from sedimentation measurements. In this method, each fraction's frequency curve is approximated by a symmetrical triangular curve, where the position of the apex of the triangle is determined by the sedimentation constant, s_0, of the fraction, and the base of the triangle is equal to $2\,s_0\left(\frac{dB}{dx}\right)$. The value adopted for the height of the triangle is such that the area of the triangle is proportional to the weight of the fraction.

Another way to construct the distribution curve has been tried by the present author (III). In this method, the distribution of each fraction is approximated by a Gaussian frequency curve for which the area is proportional to the weight of the fraction, and the standard deviation $\sigma = \frac{s_0\left(\frac{dB}{dx}\right)}{\sqrt{2\pi}}$. Before use the $\left(\frac{dB}{dx}\right)$-values have to be corrected for the influence of diffusion on the broadening of the sedimentation curve, according to a method given by the present author (III). It has been shown by this method that the different fractions overlap each other almost everywhere, but that the distributions calculated by the three methods are in reasonable agreement with each other (III). As the first method is much easier than the other two, it has been chosen here.

The ultracentrifugal technique has also been used to give a direct determination of the mass distribution of the initial polymer without any preceding fractionation. The method of deriving the mass frequency curve from the experimental refractive index gradient curve, obtained by a run in the ultracentrifuge, was first used by *Signer* and *Gross*, and further developed by *Baldwin* and *Williams*. The complications from the use of organic solvents have been treated by the present author and a new method introduced to overcome these. Details concerning the method used to analyse the sedimentation curve have been given elsewhere (IV).

A comparison of the results from precipitation fractionation and from sedimentation analysis can be made from Figures 3 and 4. In the first case, the molecular weights of the different fractions were determined by viscosity measurements and use of the equation (V)

$$\log [\eta] = 0.659 \log M - 3.823;$$

in the second case, the mass distributions over the different sedimentation constants, obtained initially, were converted to mass distributions over the different molecular weights by use of the equation (V)

$$\log s_0 = 0.484 \log M - 1.517$$

The two methods give essentially the same result. Sedimentation analysis seems, however, systematically to give somewhat narrower distri-

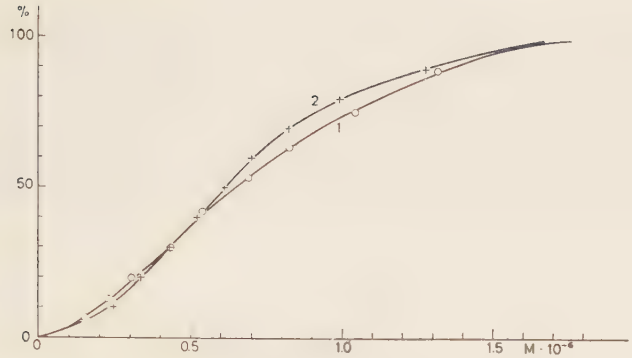

Fig. 3. Mass-distribution curve for polymer B(711)
Curve 1 determined by fractional precipitation
» 2 » » sedimentation analysis

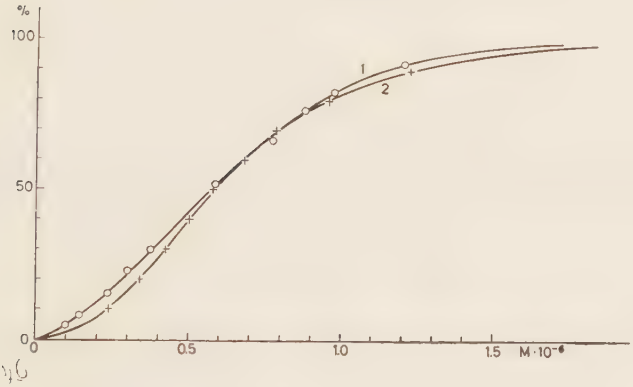

Fig. 4. Mass-distribution curve for polymer B(708)
Curve 1 determined by fractional precipitation
» 2 » » sedimentation analysis

butions. Compare also the mass distributions discussed in reference (IV). The uncertainty in the drawing of the base-line in the sedimentation diagram possibly causes a part of this discrepancy.

Theoretical mass distributions.—In the initial stage of the polymerization the rate of the reaction can be given by the following equations:

$$\frac{d\,[A_1]}{dt} = (IR) - k_p\,[M]\,[A_1] - k_t\,[A_1] \sum_{n=1}^{\infty} [A_n]$$

$$\frac{d\,[A_2]}{dt} = k_p\,[M]\,[A_1] - k_p\,[M]\,[A_2] - k_t\,[A_2] \sum_{n=1}^{\infty} [A_n]$$

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. . . . . .

$$\frac{d[A_r]}{dt} = k_p[M][A_{r-1}] - k_p[M][A_r] - k_t[A_r]\sum_{n=1}^{\infty}[A_n]$$

where (IR) denotes the rate of initiation, $[A_1]$, $[A_2]$, . . . , $[A_r]$ the concentrations of growing radicals with the degree of polymerization 1, 2, . . . r respectively, k_p and k_t are the rate constants for chain growth and chain termination, respectively. If a steady state is assumed, the above equations are all equal to zero giving:

$$(IR) = k_t\left[\sum_{n=1}^{\infty}[A_n]\right]^2 \tag{7}$$

$$[A_1] = \frac{(IR)}{k_p[M] + \sqrt{k_t(IR)}} \tag{8}$$

$$[A_2] = \frac{k_p[M](IR)}{\left(k_p[M] + \sqrt{k_t(IR)}\right)^2} \tag{9}$$

$$[A_r] = \left[\frac{k_p[M]}{k_p[M] + \sqrt{k_t(IR)}}\right]^r \frac{(IR)}{k_p[M]} \tag{10}$$

In the case of termination of the chain growth by disproportionation, the rate of formation of "dead" polymer molecules with the degree of polymerization r is

$$\frac{d[P_r]}{dt} = k_t[A_r]\sum_{n=1}^{\infty}[A_n] \tag{11}$$

The change in monomer concentration is expressed by

$$-\frac{d[M]}{dt} = k_p[M]\sum_{n=1}^{\infty}[A_n] \tag{12}$$

A combination of the last three equations gives

$$-\frac{d[P_r]}{d[M]} = \left[\frac{k_t(IR)}{k_p^2[M]^2}\right]\left[\frac{k_p[M]}{k_p[M] + \sqrt{k_t(IR)}}\right]^r \tag{13}$$

If the growing radicals are deactivated by combination instead of disproportionation equation (11) has to be replaced by

$$\frac{d[P_r]}{dt} = \frac{1}{2}k_t\sum_{s=1}^{r-1}[A_{r-s}][A_s] \tag{14}$$

and consequently

$$-\frac{d[P_r]}{d[M]} = \frac{(r-1)}{2}\left[\frac{k_t(IR)}{k_p^2[M]^2}\right]^{3/2}\left[\frac{k_p[M]}{k_p[M] + \sqrt{k_t(IR)}}\right]^r \tag{15}$$

Knowing the dependence of (IR) on the monomer concentration, it is possible to integrate equations (13) and (15), and to calculate the theoretical mass distribution for the two cases of deactivation. This has been done for redox polymerization of poly (methyl methacrylate) (II). At the first moment of the polymerization, the mass frequency function takes the form of np^n and $n(n\text{-}1)\,p^n$ in the cases of termination by disproportionation and combination, respectively.

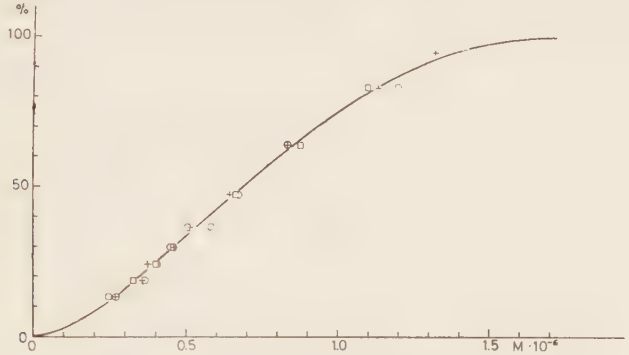

Fig. 5. Mass-distribution curve for polymer B(704)

+ = molecular weight calculated from the sedimentation constant s_0 and the diffusion constant D_A

○ = molecular weight calculated from the sedimentation constant s_0 and the diffusion constant D_M

□ = molecular weight calculated from intrinsic viscosity

For the case when both kinds of termination reactions occur simultaneously, the expression $\frac{d\,[P_r]}{d\,[M]}$ can be derived in a similar way as above, the initial mass frequency function being of the form (I) $a\,np^n + b\,n\,(n-1)\,p^n$. For the present purpose it is, however, sufficient to recognize that the relative amount of a molecular species (n) in the polymer decreases with increasing n when the polymerization proceeds, i. e., [M] decreases.

Experimental mass distributions. The compositions of polymers obtained during the first stationary stage of the polymerization reaction are illustrated in Figs. 3, 4 and 5. (See also Table 2.) The three polymers — designated by B(711), B(708) and B(704) — have all been polymerized at 60° C, and with the same amount of benzoyl peroxide. The degrees of conversion are 5.18, 9.07 and 18.1 per cent, respectively.

The polymer with a degree of conversion of 9 per cent does not contain so many high polymer species as the polymer isolated at 5 per cent conversion. This is in agreement with the preceding theoretical consideration. The decrease in the amount of high polymer species due to a decrease of monomer is, however, soon balanced by the drop in rate of termination because of the increasing viscosity of the reaction medium.

The two polymers, B(711) and B(704), have almost the same mass distribution, although the first was obtained during the initial part of the stationary state period and the second at the very end of this period of the polymerization. In spite of the fact that the 'over all' distributions are the same for these two polymers, there is a marked difference in the composition of the polymer molecules formed at the two different degrees of conversion. This will be clear if the mass distributions for the fractions of the total polymer that have been formed between 0 to 5.18, 5.18 to 9.07 and 9.07 to 18.1 per cent conversion are compared.

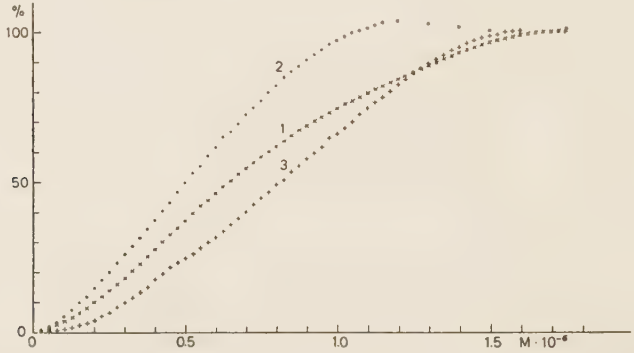

Fig. 6. Calculated mass distributions for the polymer formed at a given degree of conversion

Curve 1 Degree of conversion from zero to 5.18
» 2 » » » » 5.18 » 9.07
» 3 » » » » 9.07 » 18.1

These distributions have been calculated from the experimentally determined distributions of samples B(711), B(708) and B(704), and are illustrated in Fig. 6. The second curve in this figure, giving the composition of polymers formed between 5.18 to 9.07 per cent conversion, shows a maximum of about 102 per cent before it finally assumes the correct value, 100. This effect is due to some error in the experimental determination of the mass distributions of samples B(711) or B(708). There is a great change in composition during the first part of the reaction (curves 1 and 2) towards lower molecular weights. A comparison of curves 1 and 3 shows that at the end of the stationary period, the amount of low molecular weight molecules is suppressed in favour of molecular species of medium size. The highest fractions in the two distributions have about the same molecular weight composition.

During the second, "explosive", part of the polymerization reaction, however, there occurs such an increase in the amount of high molecular weight species, that the mass frequency function develops two maxima. The first of these two maxima is situated at the same place as the single peak is in the mass frequency curve at low conversion. The two peaks are most pronounced at intermediate degrees of conversion.

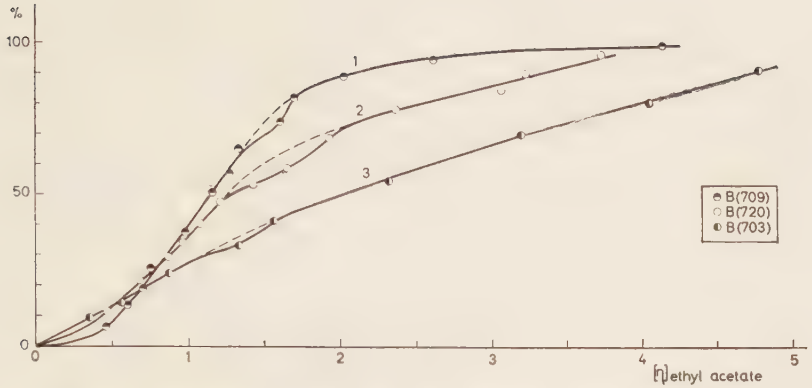

Fig. 7. Mass-distributions over the different intrinsic viscosities
Curve 1 obtained after 24.3 per cent degree of conversion
» 2 » » 72.4 » » » » »
» 3 » » 90.1 » » » » »
Polymerization temperature 60° C.

During the third part of polymerization, when the rate of polymerization gradually ceases due to lack of monomer, the distribution flattens out—the final distribution being two or three times as broad as the initial one. See the tables of fractionation data and Fig. 7, showing the

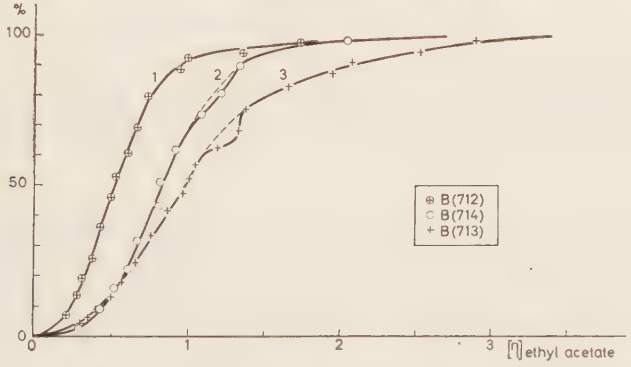

Fig. 8. Mass-distribution over the different intrinsic viscosities
Curve 1 obtained after 47.4 per cent degree of conversion, high initiator concentration
» 2 » » 13.7 » » » » » low » »
» 3 » » 41.3 » » » » » » » »
Polymerization temperature 80° C.

mass distributions over the different intrinsic viscosities for samples B(709), B(720) and B(703), isolated at, respectively, 24.3, 72.4 and 90.4 per cent conversion.

All the polymers hitherto discussed have been prepared in the presence of the same amount of initiator and at the same temperature. Fig. 8 shows some distributions for polymers polymerized at 80° C. The left

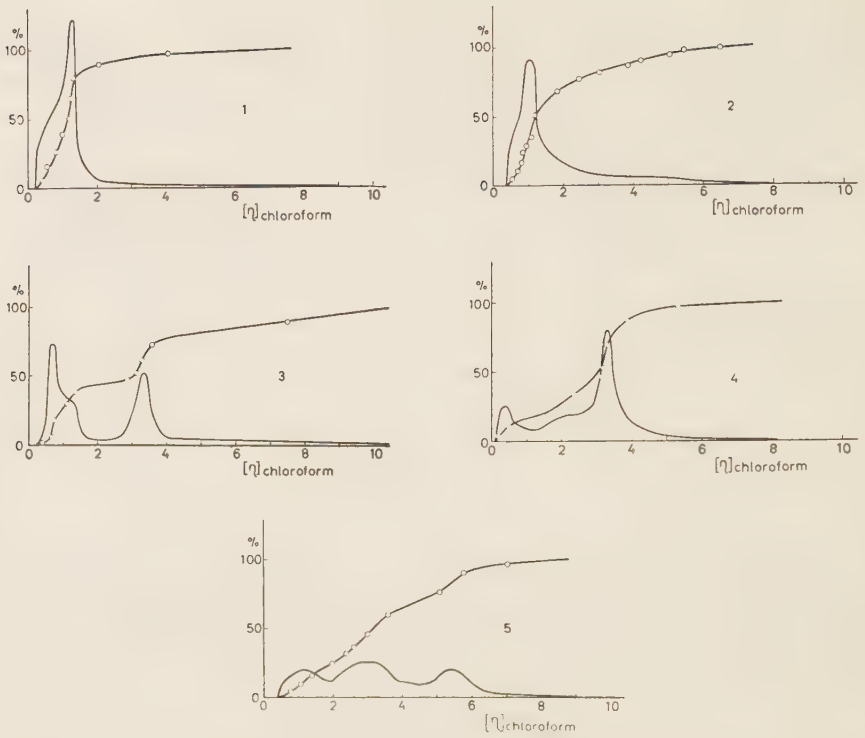

Fig. 9. Mass-distribution and mass-frequency curves of samples of poly (methyl methacrylate) taken at degrees of conversion of 11.2 (1), 28.4 (2), 53.2 (3), 83.2 (4), and 93.6 (5) per cent respectively. Intrinsic viscosity determined in chloroform.

of these curves has been obtained for a polymer prepared in the presence of the same amount of initiator as previously used. The degree of conversion is, in this case, 47.4 per cent —probably corresponding to the middle part of the "explosive" stage. The distribution curve is, in spite of this, quite smooth and, moreover, all fractions except the two highest belong to the region where the linear relationship in the $\log s_0 - \log [\eta]$-plot holds. This is in qualitative agreement with the Norrish-Smith theory that predicts a smaller change in average molecular weight, if the polymerization is performed under such circumstances that a low molecular weight polymer is formed.

If, however, the amount of initiator is decreased, the same broadening and the appearance of a jump in the mass distribution occur. See the distributions of the polymers B(714) and B(713) in Fig. 8 and Tables 4 and 5 corresponding to a degree of conversion of 13.7 and 11.3 per cent respectively.

Experimental mass distributions obtained by polymerization at 80° C have previously been published (I). In those cases, the degrees of poly-

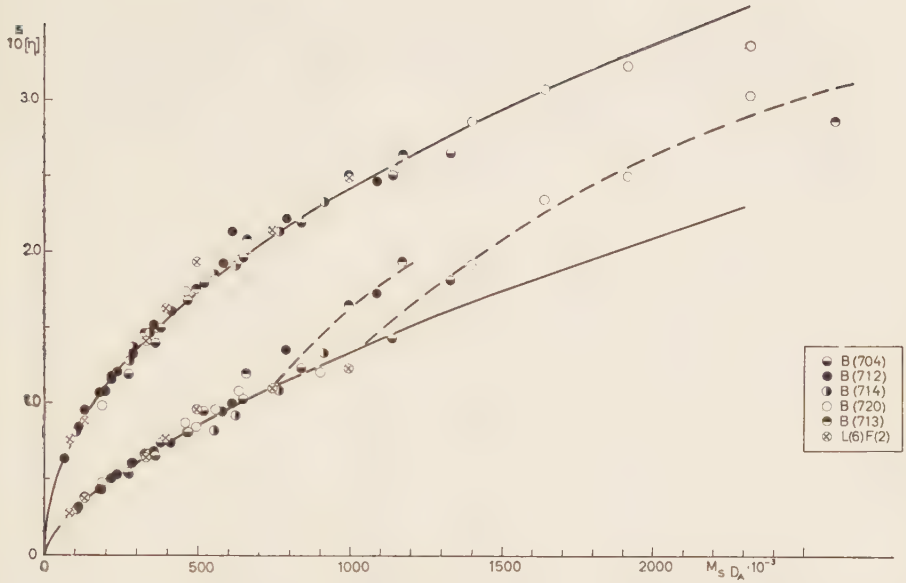

Fig. 10. s_0 and 10 $[\eta]$ as functions of M_{sD_A}. The solid lines are the curves representing the equations

$$\log s_0 = 0.48_4 \log M_{sD_A} - 1.51_8$$

$$\log [\eta] = 0.65_9 \log M_{sD_A} - 3.82_2$$

The dotted lines are drawn through points that give a curved $\log s_0 - \log [\eta]$ line. Upper curve s_0, lower curve $[\eta]$. L(6) F(2) redox polymerization.

merization were 11.2, 28.4, 53.2, 83.2 and 93.6 per cent, respectively. The concentration of initiator was not the same as for B(714) and B(713) and, moreover, the intrinsic viscosities were determined in chloroform. These older measurements also gave a doubly peaked mass frequency curve at medium degrees of conversion. The distributions were flattened out at the end of the polymerization process. See Fig. 9.

Redox polymerization of methyl methacrylate. The polymerization of methyl methacrylate in water solution and in the presence of a redox system has been treated in two earlier papers (II, III). In the first of these, some questions concerning the theoretical and experimental mass distribution have been discussed. The second paper gives the results from sedimentation, diffusion, and intrinsic viscosity measurements on some fractions obtained with this polymerization technique. The temperature dependence of the intrinsic viscosity was also investigated. In this paper, however, it was assumed that there was no concentration dependence of the diffusion coefficient. The later investigations, that have been extended both to higher concentrations and to fractions with higher molecular weights, have revealed that this assumption was not quite

true. In order to be able to compare the results from redox polymerization with the results obtained from bulk polymerization, the molecular weights of the former have been recalculated assuming the same concentration dependence of the diffusion coefficient as was found for the bulk polymers (V). The hydrodynamic behaviour of the polymer prepared by redox polymerization is the same as that of low conversion bulk polymers, see Figs. 2 and 10 and Tables 6 and 7.

Table 2. Fractionation data for polymer B(711), B(708) and B(704).

Fraction		$\frac{1}{2}n_i + \sum_{j}^{i-1} n_j$ in per cent	$[\eta]$	$M_\eta \cdot 10^{-3}$	$M_{sD_m}\,10^{-3}$	$M_{sD_A}\,10^{-3}$
B(711)	I	98.66	—	—		
	II	89.49	1.62	1,316		
	III	75.44	1.39	1,043		
	IV	63.58	1.19	824		
	V	53.39	1.06	691		
	VI	42.12	0.90	539		
	VII	29.88	0.78	434		
	VIII	19.99	0.62	306		
	IX	12.68	0.51	228		
	X	6.58	0.39	152		
	XI[1]	1.71				
B(708)	I	92.60	1.53	1,206		
	II	82.71	1.33	975		
	III	77.08	1.24	877		
	IV	66.42	1.14	772		
	V	52.16	0.95	585		
	VI	39.76	0.84	486		
	VII	29.86	0.71	376		
	VIII	22.67	0.61	299		
	IX	14.70	0.52	235		
	X	7.57	0.38	146		
	XI	4.26	0.29	97		
	XII[1]	1.54	—	—		
B(704)	I	98.56		1,950		
	II	94.90		1,580	1,425	1,324
	III	83.20		1,100	1,200	1,135
	IV	64.05		877	834	834
	V	47.57		662	671	645
	VI	36.50		585	506	515
	VII	29.84		460	447	462
	VIII	24.21		401	402	375
	IX	18.80		329	364	357
	X	13.16		248	269	269
	XI[1]	4.83		—	—	—

[1] Evaporation residue.

Table 3. Fractionation data for polymer B(709), B(720) and B(703)

Fraction		$\frac{1}{2} n_i + \sum_{j}^{i-1} n_j$ in per cent	$[\eta]$	s_0	$M_\eta \cdot 10^{-3}$	$M_{sD_m} 10^{-3}$	$M_{sD_A} 10^{-3}$
B(709)	I	99.72	4.14	—	5,460		
	II	95.11	2.62	34.8	2,730		
	III	89.23	2.03	—	1,850		
	IV	82.16	1.70	—	1,420		
	V	74.41	1.61	—	1,300		
	VI	65.24	1.33	—	975		
	VII	57.32	1.27	—	909		
	VIII	50.78	1.16	—	793		
	IX	37.81	0.98	19.1	614		
	X	25.70	0.75	16.3	409		
	XI	19.03	0.70	—	368		
	XII	13.44	0.60	13.3	292		
	XIII	6.54	0.46	10.7	—		
	XIV[1]	1.58	—	—	—		
B(720)	I	96.99	3.73			—	—
	II	90.64	3.23			—	—
	III	85.01	3.07			1,965	2,316
	IV	78.23	2.37			1,584	1,634
	V	68.70	1.93			1,304	1,395
	VI	59.02	1.65			1,021	1,141
	VII	53.12	1.43			—	—
	VIII	47.75	1.21			894	898
	IX	40.27	1.08			678	631
	X	34.39	0.96			555	553
	XI	29.39	0.87			433	456
	XII	21.70	0.68			353	356
	XIII	11.37	0.47			180	185
	XIV[1]	3.10	—			—	—
B(703)	I α	91.77	4.78	55.1			
	I β	81.03	4.05	50.5			
	I γ	70.36	3.20	—			
	I δ	54.68	2.32	29.9			
	I ε	41.59	1.56	—			
	II	33.11	1.33	—			
	III	23.95	0.87	17.9			
	IV	14.24	0.56	—			
	V	9.20	0.35	—			
	VI[1]	3.81	—	—			

[1] Evaporation residue.

Table 4. Fractionation data for polymer B(712)

Fraction		$\frac{1}{2}n_i + \sum_j^{i-1} n_j$ in per cent	$[\eta]$	$M_{sD_m}\,10^{-3}$	$M_{sD_A}\,10^{-3}$
B(712)	I	97.68	1.74	975	1,082
	II	94.08	1.36	753	785
	III	92.33	1.00	590	608
	IV	88.56	0.95	571	578
	V	79.48	0.74	393	408
	VI	69.20	0.67	369	354
	VII	60.76	0.61	291	284
	VIII	53.01	0.53	228	233
	IX	46.00	0.50	214	214
	X	36.08	0.43	177	176
	XI	25.68	0.38	130	128
	XII	19.01	0.31	109	108
	XIII	13.40	0.28	—	—
	XIV	6.91	0.21	65	62
	XV[1]	1.54	—	—	—

Table 5. Fractionation data for polymer B(714) and B(713)

Fraction		$\frac{1}{2}n_i + \sum_j^{i-1} n_j$ in per cent	$M_{sD_m}\,10^{-3}$	$M_{sD_A}\,10^{-3}$	$[\eta]$	s_0
B(714)	I	98.31	—	—	2.05	
	II	89.65	879	907	1.34	
	III	80.69	—	—	1.22	
	IV	73.72	770	763	1.09	
	V	61.59	633	621	0.92	
	VI+VII	51.09	527	550	0.82	
	VIII	42.72	457	461	0.81	
	IX	31.66	360	338	0.67	
	X	21.93	290	286	0.61	
	XI	15.72	264	272	0.52	
	XII	8.94	180	182	0.43	
	XIII	2.35	103	102	0.29	
B(713)	I	99.72	—	—	—	—
	II	98.18	2,575	2,594	2.90	41.8
	III	96.77	—	—	—	—
	IV	94.40	1,785	1,910	2.53	32.6
	V	91.10	—	—	2.08	
	VI	87.28	1,087	1,167	1.95	26.6
	VII	82.79	964	991	1.66	25.2
	VIII	75.33	—	—	1.38	23.5
	IX	68.10	—	—	1.33	—
	X	62.62	617	656	1.20	20.9
	XI	56.84	—	—	1.05	20.9
	XII	52.17	—	—	1.01	19.3
	XIII	47.34	—	—	0.97	20.1
	XIV	41.66	471	490	0.87	17.6
	XV	33.33	—		0.76	—
	XVI	24.38	323	322	0.66	14.6
	XVII	17.79	—	—	0.57	12.6
	XVIII	12.90	214	214	0.50	11.8
	XIX	8.96	—		0.40	
	XX	6.34	—		0.35	
	XXI	4.31	—	—	0.30	
	XXII	1.79[1]	—			

[1] Evaporation residue.

Table 6. Fractionation data for polymer L(6) F(2).

Fraction		$\frac{1}{2} n_i + \sum_{j}^{i-1} n_j$ in per cent	$[\eta]$	s_0	$M_{sD_m} 10^{-3}$	$M_{sD_A} 10^{-3}$
L(6) F(2)	I	94.62	1.24	25.0	965	993
	II	84.56	1.10	21.5	751	741
	III	73.60	0.96	19.4	502	493
	IV	61.57	0.77	16.3	369	392
	V	46.45	0.64	14.1	328	328
	VI	27.46	0.49	11.7	—	—
	VII	14.65	0.37	8.8	132	129
	VIII	7.95	0.27	7.6	89	79
	IX	2.23	—	—	—	—

Table 7. Showing the constants in the relationship among s_0, $[\eta]$, M_{sD_A}, and M_{sD_m}

$$\log s_0 = 0.51 \log M_{sD_m} - 1.66$$
$$\log s_0 = 0.49 \log M_{sD_A} - 1.54$$
$$\log [\eta] = 0.65 \log M_{sD_m} - 3.76$$
$$\log [\eta] = 0.62 \log M_{sD_A} - 3.61$$
$$\log s_0 = 0.78 \log [\eta] + 1.31$$

Summary

The mass distributions of poly (methyl methacrylate)s have been determined for polymers prepared under various polymerization conditions with respect to polymerization temperature, concentration of initiator, degree of conversion and polymerization technique. In bulk polymerization, a doubly peaked mass frequency curve was obtained in those cases where the conditions for a sudden increase in rate of polymerization were favoured, the two maxima being most pronounced at medium degrees of conversion. A non-linear relationship between $\log s_0 - \log [\eta]$ has been found for high molecular weight fractions. In the region of a linear $\log s_0 - \log [\eta]$-relation, the ratio $s_0[\eta]^{1/3}/M^{2/3}$ shows a definite tendency to increase with increasing molecular weight. The two anomalies in the hydrodynamic behaviour have been interpreted by assuming a change in configuration of the polymer molecules.

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